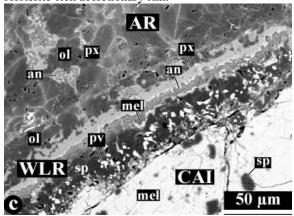
NEBULA MODELS OF NON-EQUILIBRIUM MINERALOGY: WARK-LOVERING RIMS. J. N. Cuzzi¹, M. Petaev², F. J. Ciesla^{1,3}, A. N. Krot⁴, and E. R. D. Scott⁴. ¹Ames Research Center (jcuzzi@mail.arc.nasa.gov); ²Smithsonian Astrophysical Observatory; ³NASA-NRC Resident Research Associate; ⁴Hawai'i Institute for Geophysics and Planetology, SOEST, University of Hawai'i at Manoa.

Introduction: The meteorite record contains several examples of minerals that would not persist if allowed to come to equilibrium with a cooling gas of solar composition. This includes all minerals in CAIs and AOAs. Their survival is generally ascribed to physical removal of the object from the gas (isolation into a large parent object, or ejection by a stellar wind), but could also result from outward radial diffusion into cooler regions, which we discuss here. Accretion of CAIs into planetesimals has also been relied on to preserve them against loss into the sun. However, this suggestion faces several objections [1]. Simple outward diffusion in turbulence has recently been modeled in some detail, and can preserve CAIs against loss into the sun [2]. Naturally, outward radial diffusion in turbulence is slower than immediate ejection by a stellar wind, which occurs on an orbital timescale [3]. Here we ask whether these different transport mechanisms can be distinguished by nonequilibrium mineralogy, which provides a sort of clock. Our application here is to one aspect of CAI mineralogy - the Wark-Lovering rims (WLR); even more specifically, to alteration of one layer in the WLR sequence from melilite (Mel) to anorthite (An) [4,5]. We suggest a scenario for WLR formation, refine the non-equilibrium preservation requirement as requiring the removal timescale to be shorter than the reaction timescale, suggest one crude metric of the reaction timescale, and compare with model calculations for a traditional nebula model. Our conclusions are that a traditional nebula model, in which CAIs form in a hot inner nebula and then diffuse outwards by nebula turbulence into cooler regions where their reaction with the gas slows, provides appropriate timescales (10³-10⁴ years) for this alteration feature.

The WLR sequence scenario: We model the WLR sequence as an inner spinel (Sp) - perovskite (Pv) "slag" layer, produced either by rapid, intense heating [6] or slower "reverse condensation" [7]. This layer is overlain by two condensation layers – the inner of Mel and the outer of Al-diopside (Px). Other layers may form on top of these by accretion of grains (forsterite) or parent body alteration (e.g., hedenbergite, andradite nepheline), which we do not discuss here. In most, but not all, WLRs, the Mel layer is partly or mostly altered to An; in rare cases, the Mel layer is unaltered. Figure 1 illustrates a typical WLR with its Mel layer nearly all replaced by An. We focus on this layer, because Mel is easily altered to An merely by addition of Si and O.

Meanwhile, the overlying layer of Px does not alter. So it makes for a simple system to analyze.

Figure 1. Type B CAI from the reduced CV chondrite Efremovka with WLR showing three main layers. AR = forsterite-rich accretionary rim.



The scenario for alteration of the Mel layer: At least three factors determine the rate at which a mineral can be altered, even assuming it is in full contact with the nebula gas. First, energetics implies that there might be an energy barrier to trigger before the reaction can proceed; this might require supercooling. We assume this will be covered in the wide temperature variation incurred during outward migration. Second, supply of altering atoms from the surrounding gas can, in principle, be slow enough to limit the reaction rate – but not for midplane densities. Third, diffusion of altering atoms into the lattice must occur in order for the minerals there to be altered. As mentioned above, consideration of the mineralogy suggests that Mel → An is the main reaction of interest, since one needs only add Si and O in relatively small proportions to accomplish this. Chemistry suggests that the Px layer doesn't alter, but altering atoms from the gas have to diffuse through it to get into the Mel. Because the diffusion of Si and O in Mel (Gehlenitic) is faster than in Px [8,9], diffusion through the Px outer "armorplate" layer sets the alteration timescale. Diffusion coefficients can be expressed as $D_0 exp(-E_0/RT) = D_0 exp(-d_0/T)$. Naturally these are for defect-free crystals, and diffusion might proceed preferentially along cracks and defects. However, at the high temperatures of this process, one suspects the Px layers are not dominated by defects and cracks when this diffusion occurs.

The nebula model: Recent nebula models show that temperatures high enough to evaporate most silicates exist in or near the terrestrial planet region in the first few 10⁵ years, at least, when CAIs were probably forming based

on their radiometric ages [10,11]. Observations support these models [12,13]. We have implemented a simple, analytical nebula model incorporating viscous dissipation as the principal source of thermal energy. Temperatures are calculated based on the energy dissipation and a simple nebula opacity law which allows for evaporation of ferromagnesian silicates at high temperatures; the model temperatures are in accord with [13]. As the model evolves over 1-2 Myr, the gas surface mass density and temperatures decrease. We release 10⁶ "tracer" particles at a temperature of 1500K, at t=0, and record their temperatures as they follow the gas flow, and diffuse in nebula turbulence down their own concentration gradients. Most are lost into the sun, with the advecting nebula gas. For the survivors found at 2-3 AU (about 10⁻³ of the initial population), we tabulate probability distribution functions (PDFs) for the time they spent at greater than some temperature T. The PDFs are shown in Figure 2. In actuality, temperatures fluctuate both downwards and upwards as the random walk proceeds. However, on the long term, temperatures decrease because particles must diffuse outwards to survive, and because the nebula is cooling. The profile for the mean particle (50% contour) can be described as $T(t) = T_0 exp(-t/t_d)$, where $t_d = 5E4$ years, and can be regarded as a longterm cooling curve for the particles, at least from the standpoint of the depth to which atomic diffusion can occur. We have developed an analytical solution for the depth L to which atoms diffuse, incorporating the temperature history of a particle and the diffusion coefficient as a function of temperature. The

expression is simply: $L = (D_o t_d/d_o)^{1/2} (T_o exp(-d_o/T_o) - T_f exp(-d_o/T_f))^{1/2},$ where T_f is the final temperature; other parameters have been defined above. Diffusion depths for these nebula evolutions are in the 10's of microns range, consistent with the thickness of the WLR layers in question. An even simpler calculation, also using nominal diffusion coefficients for Si and O through Px [8,9]), but at constant temperature, indicates the times needed for Si and O to diffuse through Px layers of given thicknesses, at given temperatures $(D_o=8E-6cm^2/sec, d_o=3.7E4 \text{ deg K}; [9])$:

$L(\mu m)$	t(1500K)	t(1300K)	t(1100K)
2	10 yr	300 yr	10^5 yr
20	$10^3 \mathrm{yr}$	$3x10^4$ yr	10^7 yr
200	10 ⁵ yr	$3x10^6$ yr	10 ⁹ yr

Summary: Outward diffusion in a cooling nebula is a natural explanation for the alteration observed in the Mel-An layer of WLRs. Rare examples with unaltered Mel layers could be due to rare, fast escapees. As objects diffuse outwards from hotter

formation regions into cooler regions, not only is diffusion of altering atoms through the lattice slower, but the supply of altering atoms goes down because there is less of the altering material in the vapor form. The particle is not remaining in a slowly cooling, "chemically adiabatic, or closed" gas. Thus, the removal timescale consistent with observed alteration could be longer in reality.

Other objects might be treated in similar ways. For instance, $Cor \rightarrow Hib$ alteration in CAIs [14,15] and Fo \rightarrow En alteration in AOAs [16] might be profitably studied in this way. Can fluffy Type A CAIs, largely composed of Mel, be explained by the alteration of more refractory condensates? Can this occur without any evidence of surface alteration to An? These questions merit some thought.

Bottom line: "Immediate" removal from a parent gas parcel merely means "on a timescale shorter than the alteration timescale". This constraint will vary with the mineralogy and temperature in question. A certain minimum amount of time might be required to produce observed alteration. In very low density flows (stellar winds) the limited supply of atoms also needs to be considered.

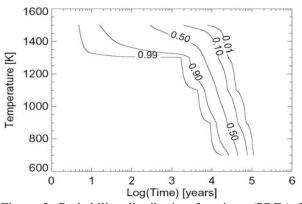


Figure 2. Probability distribution functions (PDFs) for time spent at greater than some temperature T, for survivors released at 1500K, and t=0.

References: [1] Wood J. A. (2004) GCA, 68, 4007. [2] Cuzzi J. N. et al. (2003) *Icarus*, 166, 385. [3] Shu F. H. et al. (1996), Science, 271, 1545. [4] MacPherson G. J. et al. (1989) in Meteorites and the Early Solar System (eds. J. F. Kerridge and M. S. Matthews), U. Ariz. Press, 746. [5] Brearley A. J. and Jones R. H. in Planetary Materials, Rev. Mineral. 36, 3-1. [6] Wark D. A. and Boynton W. V. (2001) MAPS, 36, 1135. [7] Wark D. A. (2004) in Workshop on Chondrites and the Protoplantery Disk, Kauai, #9050. [8] Ryerson F. J. and McKeegan K. D. (1994) GCA, 58, 3713. [9] Dimanov A. et al. (1996) GCA, 60, 4095. [10] Bell K. R. (1997) ApJ, 486, 372. [11] Cassen P. M. (2001) MAPS, 36, 671. [12] Woolum D. and Cassen P. M. (1999) Meteoritics, 34, 897. [13] Muzzerole J. et. al. (2004) ApJ, 597, L149. [14] Simon S. B. et al. (2002) MAPS, 37, 553. [15] Krot A. N. (2001) MAPS, 36, A105. [16] Krot A. N. et al. (2004) GCA, 68, 1623.